HERMANN'S PHENOMENON

BY

G. S. WALPOLE, D.Sc., F.I.C.

Hermann's Phenomenon.

By GEORGE STANLEY WALPOLE, D.Sc., F.I.C., Wellcome Physiological Research Laboratories, Herne Hill, London, S.E.

In 1887, Hermann* published an account of some experiments from which he drew the conclusion that when an electric current passed from a dilute solution of a salt, such as sodium sulphate, to one more concentrated, a liberation of acid took place at the boundary layer between the two fluids; also, that when the current passed in the opposite direction alkali was liberated at the same place. His experimental difficulties were considerable, but the facts were firmly established, though it is only to be expected that their repetition and amplification to-day should suggest another interpretation to that put forward 27 years ago.

Strangely enough, although these phenomena were cited by early physio-

---

* 'Göttinger Nachrichten,' 1887.

logists as affording an explanation of the " electrical taste,"[*] they have quite escaped all the later text-books and articles on physico-chemical subjects. Rosenthal's experiments, which showed that the " electrical taste " was not to be attributed directly to electrolytic phenomena, may have led to a general but mistaken impression that Hermann's observations were faulty. In explaining the habits of certain free-swimming protozoa, however, Dale has attributed the directive stimuli to these boundary effects. The cogency of these speculations is in striking contrast to the earlier applications of Hermann's experiments to physiological problems. In a paper on the cataphoresis of ferments, too, V. Henri has alluded to the liberation of alkali and acid at the boundaries of the ferment solution and distilled water when an electric current is passed. This, as he remarks, cannot be avoided by the use of non-polarisable electrodes, but may be overcome by dialysing the enzyme solution until it has the same conductivity as the distilled water employed. It may be pointed out, in passing, that this undesirable restriction to the experimental conditions is not necessary; it is only essential that the specific conductivities of the two solutions should be the same. But, since the published work in which this precaution has not been taken would otherwise be not properly understood, it was decided to investigate the significance of these boundary complications in their relationship to transport experiments generally.

This enquiry, the results of which are discussed elsewhere, involved experiments made to confirm and amplify Hermann's original observations, and establish them as far as possible on a quantitative basis. A rational explanation of them in terms of the hypothesis of electrolytic dissociation resulted, and the matter of this curious phenomenon assumed a sufficient interest to suggest its separate publication.

Apparatus and Method of Experiment.

For all the experiments described in this communication a transport apparatus made entirely of glass in one piece was used. The preliminary observations which led to its permanent adoption have not been described; where they were instructive they have been repeated under the better conditions afforded by this improved arrangement.

A rigid wooden stand screwed to the bench held the apparatus. The fitting was done carefully once and for all so that it could at any time be removed for filling, cleaning, etc., and replaced in exactly the same position.

The dimensions were chosen so that after the passage of the current reasonably large volumes of the fluid are available for examination. The

* Biedermann, 'Electro-physiology,' vol. 2 (1908).

bore throughout was 10 mm., except at the taps, where it was 9 mm. Full-bore taps could not be obtained. The diagrams represent in elevation and in section the apparatus ready for an observation. It has been filled and the current is about to be turned on.

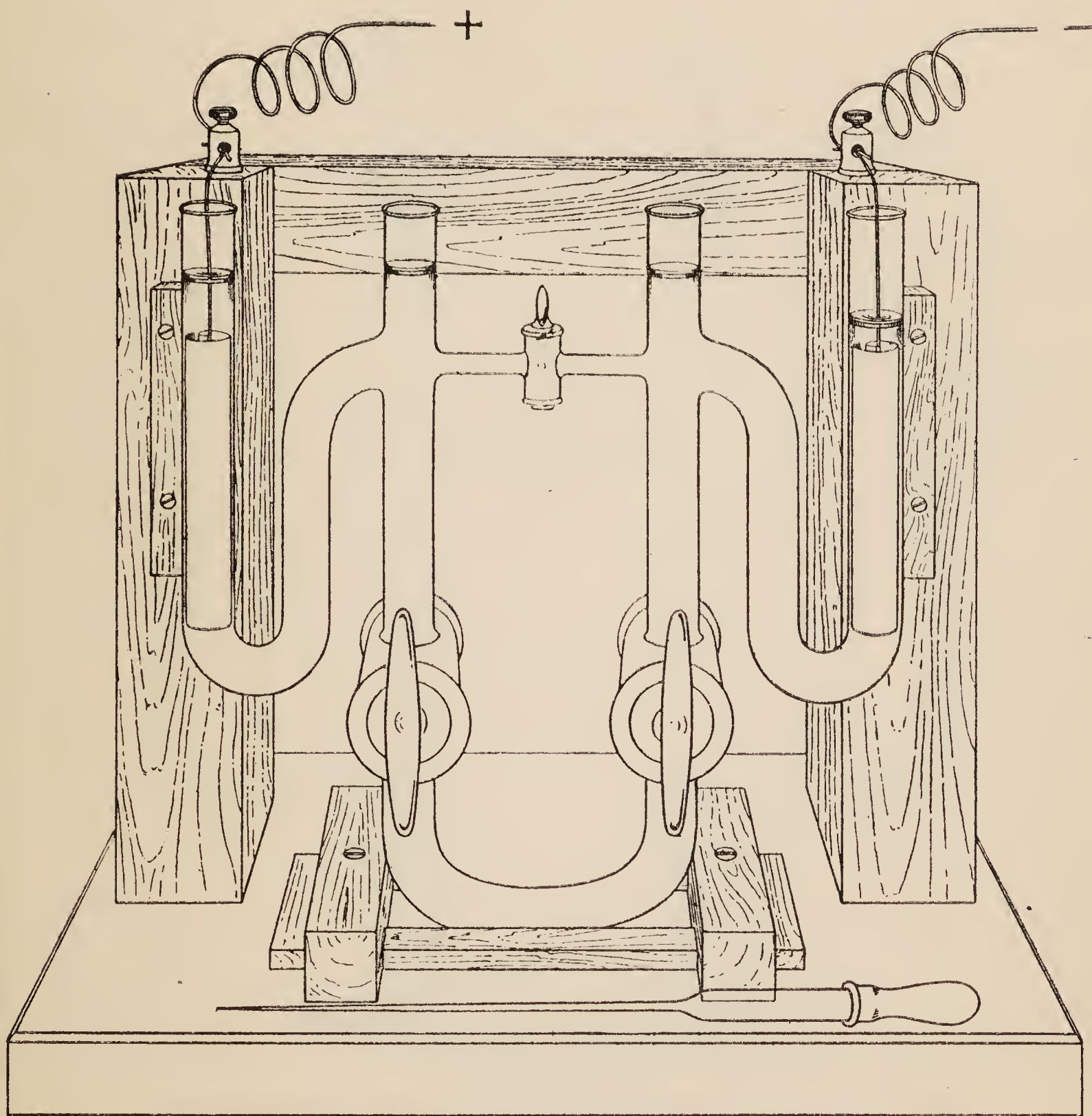The filling of the apparatus takes only a few minutes; the problem is

Fig. 1.—Perspective view of apparatus. (Half scale.)

simply to introduce four fluids, indicated in the sectional drawing, in such a manner that the boundary layers between them are sharply defined, and occupy certain positions which are exactly the same in consecutive experiments. After taking it in the hand with all three taps open, and rinsing it out with distilled water, the tube M and the lower parts of C and D (fig. 2), are rinsed, and then filled, with the "middle fluid." Any stray air bubbles

clinging to the glass are gently removed and the large taps shut. The fluid which is to occupy C and D is now used to rinse the excess of " middle fluid " out of the apparatus, which is then placed in position in the wooden stand.
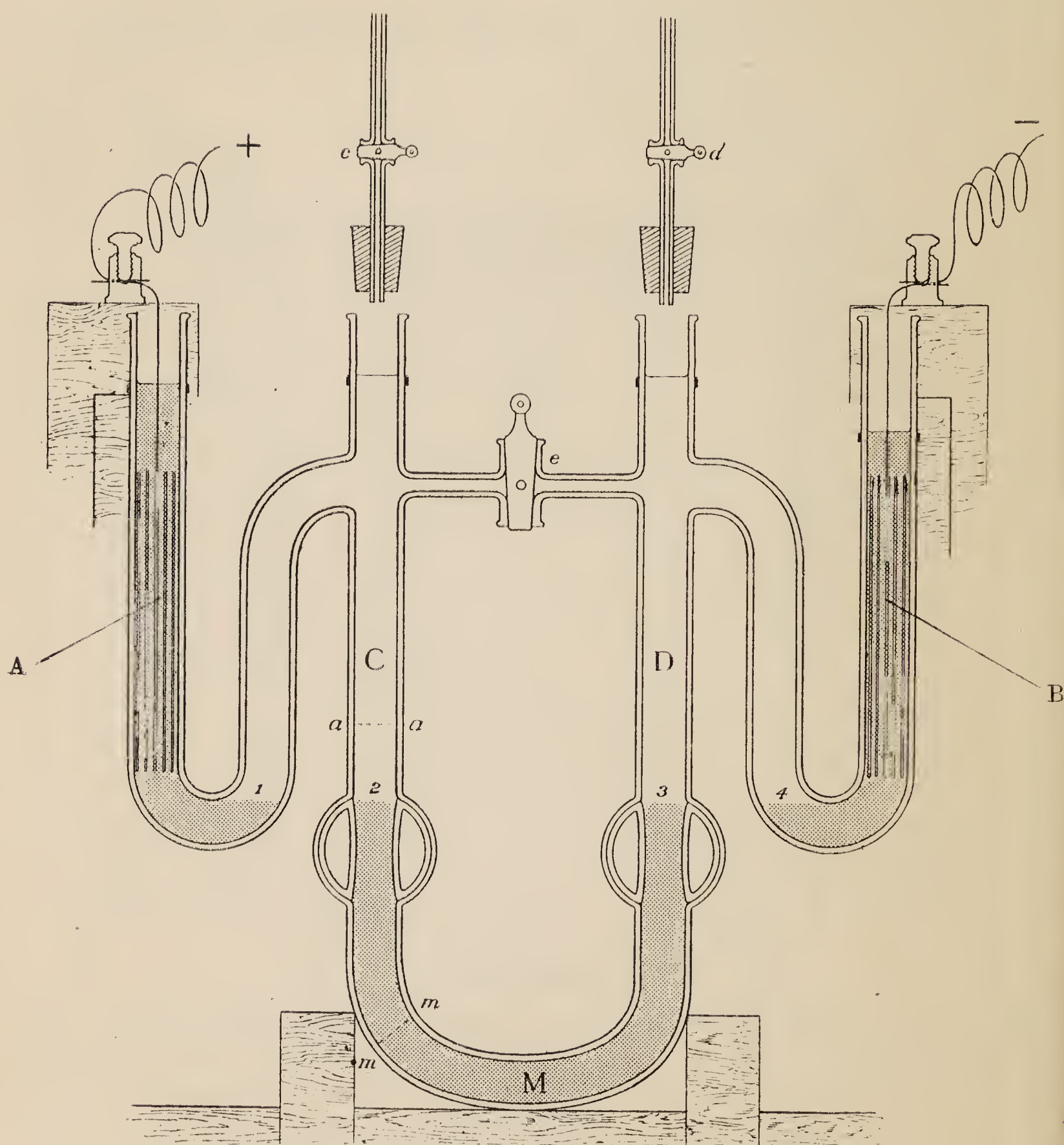

FIG. 2.—Section of apparatus.   (Half scale.)

A. Silver anode in normal sodium chloride.   B. Copper cathode in cupric chloride.

" Side tube fluid " is poured in until it reaches a mark 15 mm. from the top of one of the four upright tubes. The small tap e is open, and by a little manipulation any air bubbles in this small transverse tube are removed. Into the tops of the tubes C and D rubber stoppers are introduced each carrying a

glass tube fitted with an open stopcock. These stopcocks are marked *c* and
d. All three small taps *c*, *d*, and *e*, are now closed, and from the anode and
cathode limbs as much fluid withdrawn by means of a suitable pipetting
arrangement as is possible without allowing air to run back into C or D.
When this is done, a spiral silver sheet anode connected by a silver wire to
the positive binding screw is introduced into the anode limb, and normal
sodium chloride run in slowly until its meniscus reaches a certain mark.
This mark is so arranged that when air is let in through *c* the column in
C does not move, for it balances that in the anode limb exactly. In a
similar fashion the cathode limb is filled with 5-per-cent. copper chloride
solution round a copper electrode. The stopcocks *c*, *d*, and *e*, are now
opened and the rubber stoppers carefully removed. The large taps are
opened with a slow even motion and *e* is shut. The result is that the
four fluids are arranged as it was desired with four sharp boundaries in
the positions indicated in the sectional drawing. The position of the " middle
tube fluid " and the " electrode fluid " are shown by stippling. The " side
tube " space is left clear. It should be noticed that the position of the
apparatus in its wooden frame has been carefully adjusted so that the
tops of the plugs of the large taps are in the same horizontal plane. The
adjustment is checked by filling M and the bores of both taps with a
coloured fluid and noting the position of the two meniscuses relative to
the plugs of the taps. The two binding screws are now put in connection
with a direct lighting main, say, at 115 volts. It is, of course, one essential
condition of these experiments that the actual current passed be so small
that even at this voltage the rise of temperature due to the heat generated
in the apparatus is insufficient to cause any appreciable convection currents.

After disconnecting again from the main the large taps are turned off very
slowly to prevent mixing of the solutions by eddy currents, and the distribution
of acid and alkali at the boundaries is investigated by one or other of the
various simple devices which suggest themselves at once. A " medicine
dropper " made of hard glass and drawn out to a long fine capillary is
convenient for introducing strong indicator solution at the desired point, for
removing liquid from a given region, or for mixing small quantities of fluid
by drawing them up successively and delivering them into a common vessel
after the manner of the bacteriologist.

If, for example, in an experiment where the " middle fluid " is 5-per-cent.
sodium chloride and the " side tube fluid " 0·05-per-cent. sodium chloride,
azolitmin dissolved in 0·05-per-cent. sodium chloride be floated upon the
meniscus of A and B, it will in a few minutes diffuse and fall down to the
four boundaries and demonstrate that, though the liquid in between has

stayed neutral, acid has been liberated at the boundaries 2 and 4, counting from left to right, where the current has passed from a dilute to a concentrated solution ; and alkali has been liberated at boundaries 1 and 3, where the current has passed from a solution more concentrated to one more dilute. Moreover, the coloured fluid will come to rest and spread out at a certain depth where it reaches a layer of fluid of a density greater than its own. The actual position of the clean-cut lower horizontal boundary of the now coloured fluid in C and D is the limit of the upward diffusion of the more concentrated salt solution, and will depend only upon the duration of the experiment. The position of this upper limit is the same whether the current is turned on or not. The effect of the current is seen in that the lowest fraction of a millimetre of the azolitmin-tinted "side tube fluid" is red in one case and blue in the other, instead of being uniformly neutral in colour. The appearance can only be taken as signifying that the uppermost limits of the region of acid and alkali liberation are horizontal and sharply defined ; they coincide with the limit of salt diffusion upward, and are to be found even several hours after the opening of the large taps, only a millimetre or two above the original position of the boundary.

In all the experiments described later, alkali and acid liberations at boundaries 1 and 4 respectively were observed, but as their discussion, except so far as the considerations referring to boundaries 2 and 3 apply, is irrelevant to this investigation they will not be referred to again.

As the result of considerable experience, it may be stated of experiments in which the connection to the 115 volt main lasts for four hours only, that a first measurement of the amounts of acid and alkali liberated may be made in the following manner. The large taps are closed very carefully, both electrode fluids are sucked out with a pipette, so that the column of liquid vertically above each tap is isolated, azolitmin solution is introduced into C and D, and the liquid stirred. The amount of azolitmin solution used is the same for each experiment, and the colours assumed after stirring indicate the quantities of acid and alkali developed. Subsequently, search for acid and alkali in the bores of the taps may be made, but under these conditions little will be found. The explanation is simple when it is recognised that the sites of development of acid and alkali are the boundaries of the concentrated and the dilute solution, and that these move upwards about 4 mm. in four hours by the ordinary process of diffusion. To detect the extremely minute traces of acid and alkali formed when the experiment has only run a few minutes, it is advisable to remove all the neutral supernatant fluid from the side tubes, except the lowest 10 mm., before adding indicator and stirring. A more complete description of the shape and

position of the region in which a change of reaction is observed, and the actual titration of the amounts of acid and alkali developed, will be given later.

1st Series of Experiments. The amounts of acid and alkali liberated bear no relation to the amount of current passed.—Using as "middle fluid" any sodium chloride solution from 0·01 per cent. to 5 per cent., the amounts of acid and alkali obtained at the boundaries were the same, as nearly as could be judged, as long as the "side tube fluids" were distilled water. Also, using 5-per-cent. sodium chloride as "middle fluid" and as "side tube fluid" a 0·05-per-cent. solution of the same salt the result was still the same, though of course the current passed was many hundred times greater in this case. In fact, the amounts of acid and alkali liberated at 100 volts in four hours were independent of the concentrations of the "middle fluid" and "side tube fluid" as long as the former conducted electricity at least 100 times as well as the latter. To avoid heat liberation and subsequent convection currents the "side tube fluid" was never more concentrated than 0·05 per cent.

2nd Series. The acid, no matter what neutral salt be used, is always liberated where the current passes from the more dilute to the more concentrated solution; the alkali is always liberated where the current passes from the concentrated solution to that more dilute.—In this series of experiments a number of neutral salts were examined. Five-per-cent. solutions were used as "middle fluid"; the same solutions 100 times diluted were taken to fill the "side tubes." In all cases acid was found at the left and alkali at the right boundary.

The neutral salts chosen were examples cited of the following groups:—

(*a*) Those whose anion and cation have approximately equal migration velocities, *e.g.*, KCl, KI.

(*b*) Those whose anion is the faster ion, *e.g.*, $MgSO_4$, K_2SO_4, NaCl, $AgNO_3$.

(*c*) Those whose cation is the faster ion, *e.g.*, $KClO_3$.

(*d*) Those whose anion migration ratio increases with dilution, *e.g.*, $MgSO_4$, NaCl, KCl, KI.

(*e*) Those whose anion migration ratio decreases with dilution, *e.g.*, $AgNO_3$.

3rd Series. Other conditions being the same, a constant amount of acid and alkali is liberated, no matter what neutral salt be used.—The individual experiments of the second series above were done in pairs. Two neutral salts were taken, and the 5-per-cent. and 0·05-per-cent. solutions of each prepared from the same sample of distilled water. They were filled into two similar transport apparatus, and connected to the same 115 D.C. main in parallel for the

same time, and then examined in the same manner. The salts were chosen from groups a, b, c, d, e above, in various combinations, but there was no indication that the effect was greater in one case than in another.

4th Series. Experiments to determine the configuration and position of the zones of acid and alkali liberation.—The upper limits of the two zones in which a change of reaction has occurred have been discovered (p. 139, paragraph 1); they coincide with the upper limits of the diffusion of the salt solution. The lower limits are found by removing fluids at different levels and testing. The taps are of assistance in doing this. The operations are tedious, but with a hard glass medicine dropper drawn out to a long fine point trustworthy information can be obtained. It is found that the acid and alkali spread down more and more, as the duration of the experiment is increased, presenting an irregular diffusion front.

The state of affairs after eight hours at 220 volts, when the two fluids are water and 5-per-cent. sodium chloride, is represented in fig. 3.
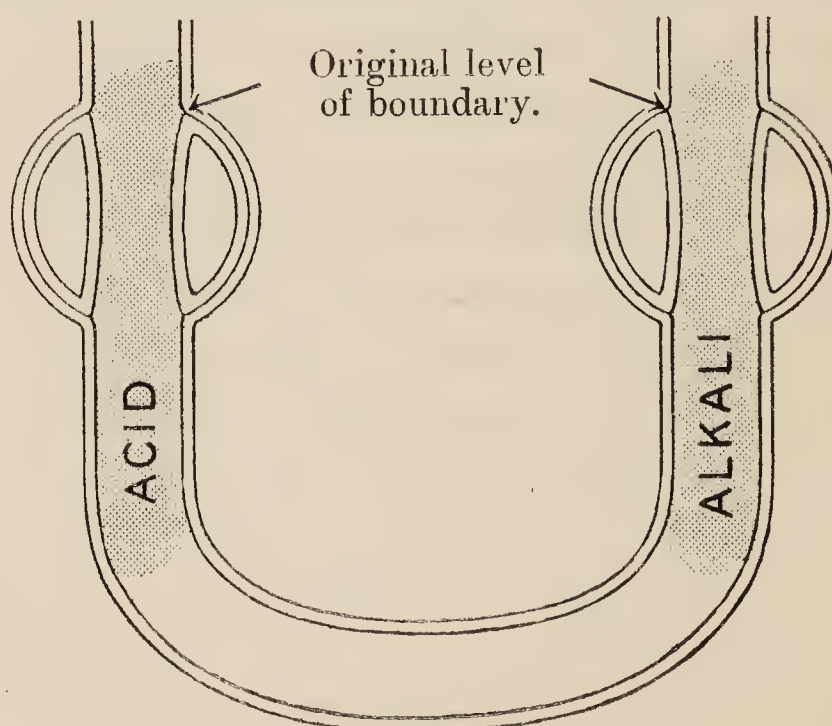

FIG. 3.

5th Series. The quantities of acid and alkali developed increase with time and then become constant.—From what has been said in the last paragraph it will be anticipated that, as the rate of acid and alkali production is very small, there will soon come a time when they diffuse downwards away from their source as rapidly as they are liberated, and that their diffusion fronts will meet. Neutralisation and consequent disappearance of the acid and alkali will occur somewhere near the middle of M as rapidly as they originate near the bottom of the side tubes.

There is every indication that this is what takes place. At 220 volts, with the apparatus of the dimensions given, this maximum is reached in about 36 hours. The quantities of acid and alkali found in the two regions increase

steadily up to this time. The time taken to reach this maximum would naturally be longer, and the maximum quantities of acid and alkali obtainable would be greater, in an apparatus made with a longer middle tube.

6th Series. Measurement by titration of the quantities of acid and alkali liberated.—The quantities are extremely small—so much so that without preliminary experience their measurement could not be undertaken. In the particular experiment chosen as affording the greatest opportunity of exact quantitative investigation, 0·25-per-cent. sodium chloride solution was surmounted by "conductivity" water. This small concentration of salt was used in the middle fluid in order to minimise the effect of the neutral salt on the indicator in the subsequent titration.

Using 115 volts, the duration of the experiment was limited to five hours, as it was known that in this time the lower limits of the acid and alkaline zones would not extend down far enough to escape their subsequent removal intact. At the end of the experiment, to avoid undue dilution of the acid and alkali, the taps were closed and the "side tube fluid" was removed except that occupying the lowest 20 mm. above the taps on either side. This was done by removing first the electrode fluids, so that the columns of liquid vertically above the taps were isolated, and then by the judicious use of a long, fine-pointed pipette. Then, opening the taps one at a time and closing either before opening the other, 4 c.c. of fluid were removed by pipette from each side of the apparatus. The experiment was performed in duplicate with two complete sets of apparatus, so that 8 c.c. of alkaline fluid and 8 c.c. of acid fluid were obtained. These two portions of 8 c.c. could, as a result of the preliminary experiments detailed, be relied upon to contain respectively the whole of the acid and alkali liberated as a result of the passage of the current. As they contained only 0·13 per cent. (*circ.*) of sodium chloride, the effect of neutral salt on the indicator could be neglected. Four beakers were taken :—

(*a*) 8 c.c. fluid from left-hand limb.

(*b*) 8 c.c. fluid from right-hand limb.

(*c*) 8 c.c. fluid Sörensen $N/15$ phosphate mixture (6·5 c.c. Na_2HPO_4 + 3·5 c.c. KH_2PO_4).

(*d*)
(*e*) } 8 c.c. of same water as used to fill the apparatus.

To each was added just enough neutral red to colour the fluid a practicable amount. This indicator was chosen because the P_H^+ range over which it shows colour change is small and extends on both sides of absolute neutrality. The tubes (*c*), (*d*), and (*e*) matched exactly. The addition of one drop of 0·001 N

caustic soda to (d) or 0·001 N hydrochloric acid to (c) caused them to turn
permanently yellow and red respectively. The contents of beaker (a) was
redder than that of (c). After the addition of 0·20 c.c. of 0·001 N caustic soda
to (a), they matched in colour ; but (a) slowly developed a pink tinge again.
By adding a further 0·10 c.c., (a) remained yellower than (c) for some minutes.
The titration of the acid liberated in each apparatus was, therefore, about
0·10 c.c., and certainly less than 0·15 c.c. of 0·001 N solution. Many experi-
ments were made to account for this small, but in proportion to the titration
volumes very large, time change. It was not understood. The control
experiments described above are evidence that it is due neither to atmospheric
carbon dioxide nor the reaction inertia of the indicator. A special experi-
ment was made, leaving the fluids in the apparatus for 24 hours without
turning on the current. It showed that it could not be attributed to alkali
from the glass.

The titration of (b) to the same tint as (c) was certainly more sharp. It
required about 0·10 c.c. of 0·001 N hydrochloric acid. The alkali liberation
in each apparatus was therefore about 0·05, and certainly less than 0·08 c.c. of
0·001 N solution.

Theoretical Interpretation of the Results Observed.

From the evidence available at this stage it is legitimate to draw the
conclusion that these boundary phenomena cannot be attributed to any
property of neutral salt solutions not common to them all. Since the most
obvious electrochemical property common to all neutral salts in solution is
that of enhancing enormously the specific conductivity of pure water when
dissolved therein, it is not surprising that this, and the hypothesis of the
dissociation of water into $H^{\cdot}$ and OH' ions, should supply the greater part of
the explanation sought. It may be noticed at once, therefore, that in either
limb of the apparatus as filled for any one of these experiments there is a
column of highly conducting solution (e.g. 5-per-cent. sodium chloride solution)
with a column of very feebly conducting solution (e.g. 0·05-per-cent. sodium
chloride solution or, even better, pure water) above it. The columns of liquid
are placed in series and in electrical connection with two points at a different
electrical potential. It follows, therefore, that the strength of the electro-
static field, which is expressed as a change of potential per unit length, is
great above the boundary and small below it. The field is downward on the
left-hand side of the apparatus and upward on the right.

Since the contents of the U-tube are at the commencement neutral
throughout, the hydrogen and hydroxyl ions per cubic centimetre are equal
in number and evenly distributed both in the dilute and in the concentrated

solution.* When the current is turned on the migration of the hydrogen ions commences in the direction of the field, while the hydroxyl ions move in the opposite direction. Migration is rapid in the dilute and slow in the strong salt solution. Hence at the left-hand boundary the number of hydrogen ions arriving in unit time from above is many times greater than the number leaving in the same time in a downward direction ; the number of hydroxyl ions leaving in an upward direction is, in similar fashion, greater than the number arriving from below. The resulting excess of hydrogen ions over hydroxyl ions accounts for the observed "acid" at this place. The development of alkali at the right-hand boundary is attributed to the accumulation of hydroxyl ions in excess of the hydrogen ions at this place by the converse process. There is one point which cannot be overlooked. The product of the H$^{\cdot}$ and OH$'$ concentrations at any point in the solutions at any time must be k_w. If the concentrations of H$^{\cdot}$ and OH$'$ resulting from the original concentrations plus ionic migration do not satisfy this relationship, then it can be assumed that a dissociation of water takes place till the relationship is again established. The dissociation may be positive or negative, but, since H$^{\cdot}$ or OH$'$ ions are liberated or disappear in equal amounts by this means, it cannot abolish the excess or deficiency of H$^{\cdot}$ or OH$'$ ions per cubic centimetre set up as a result of ionic migration in the manner suggested.

As pointed out by Dr. C. J. Martin while discussing this explanation, an accumulation of H$^{\cdot}$ or OH$'$ ions in any region, though a convenient expression, cannot be regarded as the whole of the phenomenon. Ions such as Cl$'$ or Na$^{\cdot}$ must be attracted electrostatically from other regions to balance them. With this addition the picture of the condition of affairs is complete, and the development of "hydrochloric acid" and "caustic soda," both, of course, highly ionised, is accounted for.

On the same lines may be explained why the upper layer of the region of changed reaction is sharply defined while the lower layer is not. Imagine at the left-hand boundary, where the diffusion front of the strong salt solution is a well marked horizontal layer, a hydrogen ion diffusing upwards ahead of its companion Na$^{\cdot}$, Cl$'$, and OH$'$ ions. It passes into a field of high intensity and is immediately forced down again. No such hindrance is met in its natural diffusion downwards ; it has, in fact, a small force helping it. This, coupled with its high natural velocity of diffusion, accounts for the discovery of acid, even after a few hours, a considerable distance below the original position of the boundary.

If these explanations of the phenomena observed are accepted, further

* The effect of the neutral salt on the dissociation constant of water need not here be considered.

problems immediately present themselves as to the finer mechanism of these changes of reaction and the energy changes at the boundaries. Their complete solution demands mathematical treatment of an advanced order.

An attempt at calculating the gross amounts of acid and alkali developed, however, say in the experiment described under the heading 6th Series, may be made at once—assuming that the explanation of the phenomena observed is correct and complete. The region of acid development, which it will be convenient to consider first, is totally included between the sections aa and mm of the apparatus. At both of these sections the fluid is neutral, even at the end of the experiment. The volume included is 4 c.c. The total gramme equivalents of ionised hydrogen which pass in across aa during the whole time of the experiment may be written at once

$$10^{-3} \times 10^{-P_H^+} \times tvae,\qquad(1)$$

where t is the time for which the experiment has run in seconds; v, the velocity of the hydrogen ion under unit potential gradient; a, the area of the cross-section; and e, the fall of potential per unit length across that section. Similarly since the migration velocity of the OH′ ion is 18/33 that of the H˙ ion, the total gramme equivalents of OH leaving the region by passing upwards across aa, is

$$10^{-3} \times 10^{-14\cdot14+P_H^+} \times t \times \tfrac{18}{33} vae.\qquad(2)$$

The migrations of H˙ and OH′ ions past the section mm are sufficiently small to be neglected, for they are smaller than those past aa in the ratio of the conductivities of water and a 0·25-per-cent. solution of sodium chloride. To restore neutrality to this region at the end of the experiment, equivalents of OH′ must be added in amount equal to the sum of these two quantities. The quantity (1) represents the OH′ ions required to neutralise the H˙ ions which have arrived ; the quantity (2), the deficiency of OH′ ions which must be made up.

Since for the titration 0·001 N caustic soda was used, the sum of (1) and (2) must be multiplied by 10^6 to give the number of cubic centimetres required. The titration should be

$$10^6\left(10^3 \times 10^{-P_H^+} \times tvae + 10^3 \times 10^{-14\cdot14+P_H^+} t \times \tfrac{18}{33} vae\right).\qquad(3)$$

Inserting the following values

$$P_H^+ = 7\cdot07,$$
$$t = 18,000 \text{ seconds},$$
$$v = 33 \times 10^{-4},$$
$$ae = 2\cdot93,*$$

* The determination of the value of the product ae, which depends on the voltage applied to the ends of the "side tubes" and upon their shape, was the object of a

the calculated value is 0·027 c.c. 0·001 N caustic soda. Expression (3) is also the expression for the volume of 0·001 N hydrochloric acid required to neutralise the alkali liberated in the region of change of reaction on the right-hand side of the apparatus. So that this titration also should be 0·027 c.c. if the assumptions made are correct. The quantities of acid and alkali found (0·15 and 0·08 c.c. of 0·001 N solution respectively), though of the same order of magnitude as those calculated, are in excess of those quantities anticipated on these suppositions, if the accuracy of these titrations can be trusted. To establish certainty that the difference between the calculated and observed values is significant would require special apparatus, water of exceptional purity, and an expenditure of time which seems scarcely justifiable.

In view of the inaccuracy of the titration of these small quantities nothing can be gained by discussion of possible reasons for the lack of agreement between the calculated and observed values, though it may be remarked that the purer the water used the sharper, smaller, and more nearly equal were the titrations observed.

On the basis of the explanation offered, therefore, the quantities of acid and alkali liberated in a typical Hermann experiment have been predicted, and found in practice, to be of the order 0·03 c.c. of 0·001 N solution. This quantity, though detectable, could not be measured with accuracy.

It may be stated, in conclusion, that invariably when an electric current passes from one aqueous solution to another of different specific conductivity, there will be either acid or alkali liberated at the boundary, depending on the direction of the current. It is widely recognised that in such circumstances a concentration of one of the ions of the feebly conducting solution

separate experiment. It is equal to E/k, where E is the potential difference between the ends of the "side tube" space, and k is their "resistance capacity." For, if the "side tubes" are filled with fluid of specific conductivity s, the current passing may be written $aes = Es/k$. By "side tubes" are meant the whole of the volume which is not stippled in diagram. The apparatus was filled in the usual manner with normal NaCl and saturated $CuSO_4$, as electrode fluids, normal NaCl as "middle fluid," and with 0·01 N KCl in the "side tubes." With 115 volts between the electrodes the current passed was 3·58 milliampères. Filling the apparatus in exactly the same way, except that 0·10 N KCl was placed in the side tubes, the current passed was 31 milliampères at the same voltage. If the resistance of the electrode fluids and the normal sodium chloride in the "middle tube," which is common to both, be written ω and the standard values of the specific conductivity of the KCl solutions be taken—

$$\omega + \frac{k}{12·3 \times 10^{-4}} = \frac{115}{3·58 \times 10^{-3}} \quad : \quad \omega + \frac{k}{11·2 \times 10^{-3}} = \frac{115}{31 \times 10^{-3}} ,$$

from which equations $k = 39·2$. Hence

$$ae = \frac{E}{k} = \frac{115}{39·2} = 2·93.$$

at the boundary will occur : but that H˙ or OH′ ions will always be found concentrated there, too, has escaped recognition.

A simple experiment can be devised to demonstrate these facts in a striking manner. The apparatus is filled, say, for the experiment under the heading 6th Series, except that, before filling, a little dry azolitmin is dissolved in the middle fluid, and, in such quantities as to produce the same tint, into the side tube fluid as well. Shortly after turning on the current, the litmus will begin to collect at boundaries 1 and 3, and to move away from boundaries 2 and 4. A space above the left-hand tap 1 or 2 mm. deep will be left perfectly clearly defined and colourless in a quarter to half-an-hour. Moreover, though this requires care in the amount of azolitmin used, the changes of colour of the litmus at the boundaries demonstrate, in addition, that at each boundary either H˙ or OH′ ions concentrate there too. The red litmus anions in the middle tube will not move at all or show any change in their even distribution indefinitely.

The analogy between the acid and alkali liberation at the boundaries of solutions of unequal conductivity (taken together with the supposed bleaching action of litmus in the regions becoming colourless in the experiment just described) led Hermann to consider the phenomena at these boundaries similar to those at metallic electrodes. He attributed them to the discharge of ions. In many experiments with potassium iodide, where, after the experiment, the boundary was tested with starch, and silver nitrate, where metallic silver was looked for, no evidence of this occurring could be found.

Summary.

At the boundary between two solutions of unequal specific conductivity a change of reaction is developed if a difference of potential be maintained between them. Alkali is liberated if the current passes from the better conducting solution to that not conducting so well : acid, if the current passes in the opposite direction. The amounts may be calculated from the potential gradients in the solutions on each side of the boundary, the time for which the difference of potential is maintained, the resistance constant of the vessel employed, the dissociation constant of water, and the known migration velocities of hydrogen and hydroxyl ions.